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(19)

(54) ELECTRO-OPTICAL DEVICE INCLUDING AN IMPROVED LIQUID CRYSTAL COMPOSITION

(71) We, HITACHI, LTD., a Corporation organised under the laws of Japan, of 5—1, 1-chome, Marunouchi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a nematic liquid crystal composition suitable for use in a device for displaying numerical figures, letters, graphs, images, etc., and more particularly to a liquid crystal display device capable of being driven by means of pulses with a short pulse width and effecting a good display in the manner of a time sharing without any flickering.

Several display devices based on the use of nematic liquid crystals have been already proposed. One of the devices utilizes a dynamic scattering mode of the nematic liquid crystal. When an electric field is applied to a film of nematic liquid crystals, the orientation of the liquid crystals is disturbed, and light beams incident onto the film layer are scattered and show a white turbidity. The intensity of transmission or reflection of the incident light beams depends upon the applied electric field. The display device utilizes this electro-optical effect, so that a desired pattern can be displayed by a change of voltage or frequency applied to the liquid crystal in accordance with an input signal. A display device of this kind has a very low power consumption and requires a relatively low operating voltage. Therefore, such a display device is useful for digital clocks, small table-type electronic computers, electrical measuring instruments, etc. Further, it is also adapted for a large scale display device, because the display panel can be made planar. However, the speed of response to a single input signal is slow, that is, the "rise time" (time from the application of the voltage until the contrast reaches 90% of saturation value) is rather poor, being as long as 10 ms (milliseconds), and the threshold voltage is also indefinite.

The simplest method for displaying a large number of segments on the same display surface is the one based on time sharing. That is, a display method for successively exciting display points at definite time intervals, relying on the persistence of the image in the human eye so that all the display points appear to be excited simultaneously.

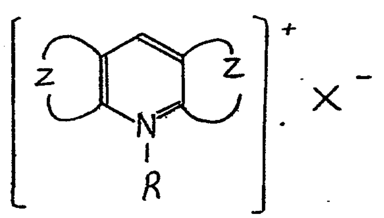
However, when liquid crystals, whose necessary time for excitation is 10 ms, are used in a display device having 8 display points using a time sharing system, a voltage must be applied to each display point for 10 ms, respectively, and thus one run of the application of the voltage to the 8 display points will require 80 ms. Thus each display point appears to flash once every 80 ms. Since the human eye perceives flickering if a flash having a decay time less than 40 ms appears at more than 40 ms intervals, simultaneous display of 8 display points, without flicker, is impossible in such a time sharing display.

To avoid flicker, nematic liquid crystals mixed with a small amount of cholesteric liquid crystals may be used. Nematic liquid crystals containing cholesteric liquid crystals have the so-called memory effect of retaining the white turbidity for a considerably long period of time, even after the applied voltage has been removed from the liquid crystal mixture. However, the liquid crystal mixture has a long rise time, and therefore the time required for the display is prolonged correspondingly. This is such a serious difficulty that an alternating current electric field of several kHz must be applied to the liquid crystal mixture in order to subsequently erase the turbidity.

In a liquid crystal display, it is an essential condition for matrix display that the threshold voltage is definite and the contrast ratio

(a ratio of the intensity of light during scattering due to the application of voltage to the intensity of light during non-scattering) changes drastically with an increase in the applied voltage.

According to the present invention there is provided an electro optical device comprising a nematic liquid crystal layer capable of effecting dynamic scattering; means for supporting said liquid crystal layer; a plurality of first electrodes for applying a pulsed electric field to said liquid crystal layer; said liquid crystal layer being divided thereby into a plurality of segments; a second electrode for applying a pulsed electric field to said liquid crystal layer, the second electrode being positioned opposite to the first electrodes, the liquid crystal layer being sandwiched between the first electrodes and the second electrodes; means for applying a pulsed electric field through the first and second electrodes to the segments of the liquid layer by time sharing, the liquid crystal layer containing an amount effective to enhance dynamic scattering motion of said liquid crystal of a compound of the formula:



(I)

wherein R is a member selected from the group consisting of alkyl group having not more than 20 carbon atoms and phenyl groups and X is a halogen atom from chlorine, bromine and iodine, and either both of Z are nothing or each forms a further benzene ring. In particular there is provided an electro optical display system utilising such a composition comprising a large number of optical segments which may be driven using a time sharing system.

Features of the present invention will be apparent from the following detailed description by way of drawings.

Figure 1 is a partially cross-sectional perspective view of an electro-optical display device to which the present invention is applied;

Figure 2 is a graph showing relations between the applied voltage and contrast ratio of the nematic liquid crystals;

Figure 3 is a view showing a model of X—Y matrix-type display elements;

Figure 4 is a graph showing relations between the applied voltage-pulse width and contrast ratio of the conventional liquid crystals;

Figure 5 is a graph showing relations between the applied voltage-pulse width and contrast ratio of the liquid crystals according to the present invention;

Figure 6 is a graph showing relations between the amount of hexadecyltrimethylammonium bromide added, and contrast ratio and rise time.

The well known, crossed lattice optical display device is shown in Figure 1 as one example of the electro-optical device, to which the present invention will be applied. However, the scope of the present invention is not restricted to such a device as illustrated in Figure 1, but it should be understood that one embodiment is shown in Figure 1 to facilitate the understanding of the present invention. Particularly since the present invention is applicable to a display device made up with a combination of a large number of segments, as will be described later.

In Figure 1, a crossed lattice optical display device 1 has a transparent glass back support plate 12 and a transparent glass front support plate 10. These two support plates are placed at a distance d of usually about 5 to 30 microns from each other, and appropriate liquid crystals (not shown in the drawing) are inserted into a space 15 between these support plates. A plurality of transparent electrodes 13a, 13b and 13c are arranged in parallel on the front support plate 10, and a plurality of transparent electrodes 14a, 14b and 14c are arranged in parallel on the back support plate 12. The electrodes 13a, 13b and 13c of the device 10 are connected to a switch 16 through connecting means 23a, 23b and 23c, respectively, and the electrodes 14a, 14b and 14c to the switch 17 through connecting means 24a, 24b and 24c, respectively. The switches 16 and 17 are connected to an earthed power source 18 through contact means 36 and 37, respectively. In the power source a pulse generator and control means are included.

In the transmission-type display device an observer is positioned at a side opposite to the light incident side. The liquid crystals at intersections of the electrodes are disturbed when a sufficiently high voltage is applied between the electrodes, and scatter the incident light. As a result, the observer can perceive that the disturbed parts are darker than other non-disturbed parts.

In the reflection-type display device, the observer is positioned at the same side as the light incident side, and observes the reflected light which is scattered by the disturbance of the liquid crystals and reflected on a reflective film formed on the inside surface (the side in contact with the liquid

crystals) of the back support plate of the display device.

As the transparent support plates, various kinds of transparent solid, such as various kinds of glass, quartz glass, transparent corundum, transparent synthetic and natural resin, etc., can be used. The transparent electrodes can be prepared by vapor-depositing, for example, indium oxide or tin oxide onto the support plates. The electrode to be formed on the reflective film may be, for example, a film of copper, aluminum, chromium or nickel.

Now, explanation will be made of characteristics of the liquid crystal composition according to the present invention.

Let us consider such a case that a matrix liquid crystal display device shown in Figure 3 is actuated, where the liquid crystals having a voltage-contrast ratio characteristic shown in Figure 2 are used. To display a segment A, a voltage is applied between the electrodes X_1 and Y_1. To obtain a contrast ratio C_1 when the liquid crystals having the characteristic shown by "a" in Figure 2, a voltage V_1 is necessary. By applying a voltage $+V_1/2$ to the electrode X_1 and voltage $-V_1/2$ to the electrode Y_1, a potential V_1 is obtained, and the segment A can be displayed with the contrast ratio. C_1. Since a voltage $+V_1/2$ is applied to a segment B and a voltage $-V_1/2$ to a segment D at the same time, the segments B and D are also displayed with a contrast ratio C_2 corresponding to the potential $V_1/2$. That is, a cross talk results in the display device.

A system based on frequency conversion has been proposed to solve this problem. That is, when an alternating current electric field with sufficiently high frequency is applied to liquid crystals, the dynamic scattering mode of the liquid crystals is quenched. In other words, an alternating current voltage with a low frequency capable of effecting the scattering is selectively applied to the parts to be displayed, whereas an alternating current voltage with a sufficiently high frequency capable of quenching the scattering is selectively applied to the parts not to be displayed. However, a circuit for the selective application of two kinds of voltages with different frequencies becomes a complicated one, and thus is not always deemed as an economical circuit.

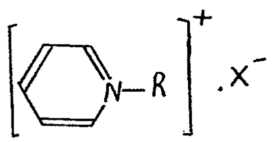
In the case of liquid crystals having the characteristic as shown by "b" in Figure 2, a voltage V_2 must be applied to obtain a contrast ratio C_1. By applying a voltage $+V_2/2$ to the electrode X_1 and a voltage $-V_2/2$ to the electrode Y_1, the segment A can be displayed with the contrast ratio C_1. At that time, voltages $V_2/2$ are applied to the segments B and D, respectively, but since such voltages are less than the threshold voltage V_s, the segments B and D undergo no scattering, that is, these segments are not displayed.

Therefore, if a liquid composition having a definite threshold voltage and a good contrast ratio-voltage characteristic as shown by "b" in Figure 2 and quick response is used, a liquid crystal display device with a clear display having no flickering, based on the time sharing, can be obtained.

The present inventors noted the fact that nematic liquid crystals have a characteristics behavior having regard to the contrast ratio characteristics varying with the pulse width of the applied voltage. In Figure 4, a contrast ratio characteristic of a liquid crystal comprising methoxybenzilidene parabutylaniline (80% by weight) and ethoxybenzilidene parabutylaniline (20% by weight) is shown when the applied voltage and the pulse width are changed (duty ratio 1/8). As is apparent from Figure 4 wherein curve 1 shows the result when using 35 volts applied voltage, curve 2 the result when using 30 volts and curve 3 the result when using 25 volts, the contrast ratio is decreased with shorter pluse width, and finally no scattering takes place at all. The similar tendencies are observed in other applied voltages. To carry out a time sharing display without flickering to human eyes, a high contrast ratio is necessary in a shorter pulse width driving. It is seen that the contrast ratio with respect to the applied voltage of 35 V (curve 1) is decreased with the reduciton in the pulse width, but a maximum appears in the contrast ratio at a pulse width of about 8 to 15 mins. That is, the contrast ratio is not always reduced directly or linearly with the reduction in the pulse width. Thus, the present inventors perceived that a time sharing display would be possible without any flickering by reference to the foregoing facts, if such liquid crystals as having a high maximum of the contrast ratio under the driving condition of low applied voltage and a short pulse width is used.

As a result of studies on various additives on the basis of the perception, the present inventors have found that a liquid crystal composition responsive to pulse driving can be obtained by adding a halide of organic quaternary nitrogen compounds, in particular pyridinium halides and acridinium halides to a nematic liquid crystal composition.

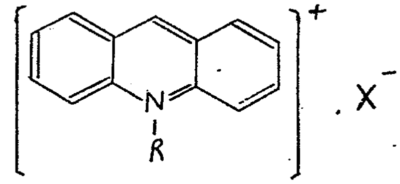
The pyridinium halides used in the present invention are pyridinium halides represented by the general formula:



(II)

wherein R represents an alkyl group having not more than 20 carbon atoms and phenyl groups and X represents a halogen atom selected from chlorine, bromine and iodine, and include, for example, 1-hexadecylpyridinium chloride, 1-hexadecylpyridinium bromide, and 1,1'-ethylenebispyridinium bromide.

The acridinium halides used in the present invention are acridinium halides represented by the general formula:



(III)

wherein R represents an alkyl group having not more than 20 carbon atoms and phenyl groups, and X represents a halogen atom selected from chlorine, bromine, and iodine, and include, for example, 10-methylacridinium chloride, and 10-methylacridinium bromide. These halides are used alone or in a mixture of two or more thereof.

Any nematic liquid crystal compound can be used, so long as they are the compounds capable of effecting dynamic scattering as the liquid crystals, for example, the nematic liquid crystals, in which the direction of dipole moment of the molecule is not identical with the direction of longitudinal axis of the molecule. It is also desirable that these liquid crystals have a liquid crystal temperature (mesomorphic temperature) at about room temperature.

The liquid crystal compounds used in the present invention include such ordinary liquid crystal compounds as p-methoxybenzylidene - p - butylaniline, p - ethoxybenzylidene - p - butylaniline, p - butoxybenzylidene - p - butylaniline, p - butoxybenzylidene - p - n - propylaniline, p - hexyloxybenzylidene - p - toluidine, p-pentyloxybenzylidene - p - toluidine, and p - heptyloxybenzylidene - p - acetoxyaniline. These liquid crystal compounds are used alone or in a mixture of two or more thereof.

A liquid crystal composition having a good responsibility to pulse driving can be obtained by adding at least 0.05% by weight of the halide of the quaternary nitrogen compound to said liquid crystal compound, based on the weight of the liquid crystal compound. However, the addition of a larger amount of the halide does not always bring about a better result, and in view of Example 8, which follows, up to about 1% by weight of the halide is the preferable range. When an amount of the halide added exceeds 1%, an impedance of the liquid crystal composition considerably decreases whereby consumption of power increases.

Now, the present invention will be described in detail by way of examples.

Examples 1—3.

0.2% by weight each of the halides of quaternary nitrogen compounds listed in Table 1, was added to methoxybenzylidene-p-butylaniline, and mixed therewith until it was completely dissolved therein. Each of the resulting liquid crystal compositions was placed on a glass plate 40 mm×50 mm×3 mm thick) vapor-deposited with an aluminum film, and a glass plate (the same size as above) deposited with a tin oxide transparent electroconductive film by spraying was placed thereon to sandwich the liquid crystal composition between these two plates, using a 9 μ-thick polyester film as a spacer, whereby a reflection-type display elements was prepared. A pulse voltage was applied to the element, using a variable pulse width voltage generator, where the transparent electro-conductive film was used as an anode.

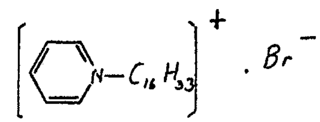
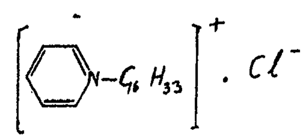
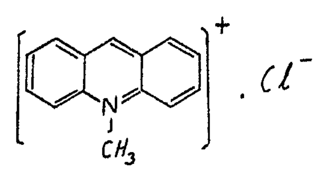
Contrast ratio was measured by applying a direct current pulse voltage of pulse width of 0.5 ms to 300 ms and voltage of 1 to 40 V, while fixing the duty ratio to 1/8. Better responsibility to short pulse width drive was obtained than when employing a conventional liquid crystal composition. Contrast ratio at plus width of 2 ms, duty ratio of 1/8 and applied voltage of 30 V are shown in Table 1.

As is apparent from Table 1, excellent contrast ratios were obtained at such a short pulse width as 2 ms in all of the Examples of the present invention. The changes in responsibility to short pulse width of the crystal liquid composition of Example 4 at the applied voltages 25, 30 and 35 V are shown by curves 4, 5 and 6, respectively in Figure 5. The contrast ratio is considerably high, and the responsibility to short width of 1 to 10 ms pulse is excellent, as compared with the conventional ones shown in Figure 4.

That is, the liquid crystal compositions exhibit the maximum of contrast ratio at a pulse widths smaller than 10 ms, which is

suitable for display of time sharing. Further, the state of display according to the time sharing was observed, and a clear display was obtained without any flickering.

TABLE 1

Ex. No.	Additive	Chemical Structure	Contrast Ratio
1	1-Hexadecylpyridinium		48
2	1-Hexadecylpyridinium chloride		25
3	10-Methylacridinium chloride		27
Conventional Example	None		1

Examples 4—8.

0.2% by weight of 1-hexadecylpyridinium chloride was added to each of the liquid crystal compositions listed in Table 2 and was completely dissolved therein. Reflection type display elements were prepared, using the resulting mixtures, in the same manner as in Examples 1—3, and responsivity to short width pulse was measured.

Contrast ratio at pulse width of 2 ms., duty ratio of 1/8, and voltage of 30 V are shown in Table 2, and excellent contrast ratios were obtained in all of Examples 4—8, as compared with the conventional Example.

A matrix display device of 5 × 7 elements comprised with strip electrodes was prepared, using the liquid crystal composition of Example 6, and was driven by the time sharing. A good display was obtained without any flickering.

TABLE 2

Example No.	Liquid crystal composition	Liquid crystal composition temperature range	Contrast
4	Methoxybenzylidene-p-butylaniline (50 parts) + 1-hydroxymethoxybenzylidene-p-butoxyaniline (50 parts)	20 – 48°C	40
5	Methoxybenzylidene-p-butylaniline (80 parts) + ethoxybenzylidene-p-butylaniline (20 parts)	10 – 47°C	35
6	Methoxybenzylidene-p-butylaniline (60 parts) + ethoxybenzylidene-p-butylaniline (40 parts)	10 – 48°C	14
7	Methoxybenzylidene-p-butylaniline (50 parts) + ethoxybenzylidene-p-butylaniline (45 parts) + methylbenzylidenebutylaniline (5 parts)	-10 – 56°C	22
8	Eutectic mixture of 4-methoxy-4'-butylazoxybenzene and 4-butyl-4'-methoxybenzene	16 – 76°C	12
Conventional Example	The same liquid crystal as in Example 8. No halide added.	10 – 47°C	1

Remark: Parts in Table 2 are by weight.

As described above, the electro-optical device obtained according to the present invention can be utilized not only as the conventional elements such as light switches and optical modulators, but also as a cheap display device according to the time sharing, because the electric circuit required is simple. Especially, the present electro-optical element is effectively utilized in an X—Y matrix type display device, where electrodes are arranged in stripes, and one set of the electrodes is crossed with another to utilize the cross-points as display points. The present electro-optical device is suitable for large scale display devices and the circuit for driving the devices can be simplified because the devices can be driven by a time sharing system.

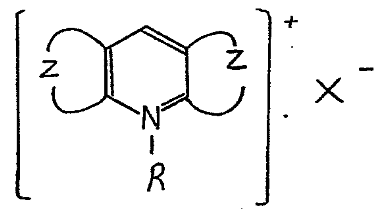
In the foregoing Examples, only reflection-type elements have been illustrated, but the present electro-optical element can be also applied to the display devices of transmission type, projection type, etc.

In the present electro-optical display device, a pulse generator is used for producing a pulse having an amplitude larger than a dynamic scattering motion limit but smaller than a discharge voltage of said liquid crystal and a pulse width smaller than 10 ms, preferably 0.5—10 ms.

In the present electro-optical display device, a means is operatively connected to said pulse generator for selectively supplying said pulse to the selected electrodes of first electrodes and second electrodes at a predetermined order for said selected electrode with a predetermined time interval in order to apply the pulsating electric field to the selected segments corresponding to said selected electrodes thereby to generate said dynamic scattering motion in the liquid crystal of the selected segments. The time interval is shorter than the period in which an intensity of observed light scattering decays to a predetermined value.

WHAT WE CLAIM IS:—

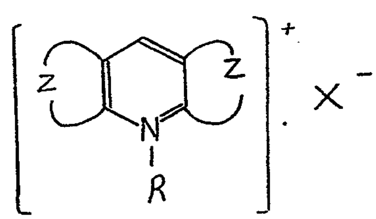
1. An electro-optical device comprising a nematic liquid crystal layer capable of effecting dynamic scattering; means for supporting said liquid crystal layer; a plurality of first electrodes for applying a pulsed electrical field to said liquid crystal layer, said liquid crystal layer being divided thereby into a plurality of segments; a second electrode for applying a pulsed electric field to said liquid crystal layer, the second electrode being positioned opposite to the first electrodes, the liquid crystal layer being sandwiched between the first electrodes and the second electrodes; means for applying a pulsed electric field through the first and second electrodes to the segments of the liquid layer by time sharing, the liquid crystal layer containing an amount effective to enhance dynamic scattering motion of said liquid crystal of a compound of the formula



wherein R is a member selected from the group consisting of alkyl groups having not more than 20 carbon atoms and phenyl groups, and X is a halogen atom selected from chlorine, bromine and iodine and either both of Z are nothing or each forms a further benzene ring.

2. An electro-optical device according to claim 1, wherein the liquid layer contains 0.5 to 1% by weight of the halides of the organic quaternary nitrogen compounds, based on the weight of the liquid crystal.

3. An electro-optical device comprising a liquid crystal layer containing nematic liquid crystals capable of effecting dynamic scattering; means for supporting said crystal layer; a plurality of first electrodes for applying a pulse voltage to said liquid crystal layer; a second electrode for applying a pulse electric field to the liquid crystal layer together with the first electrodes, the liquid crystal layer being sandwiched between said first and second electrodes; means for selecting an electrode to be applied with an electric field thereby resulting in an electric field being applied to the liquid crystal layer in a desired sequence through desired ones of the plurality of electrodes forming the plurality of first electrodes, wherein the liquid crystal layer contains an effective amount to enhance dynamic scattering motion of said liquid crystal of at least one halide of at least one organic quaternary nitrogen compound of the formula:



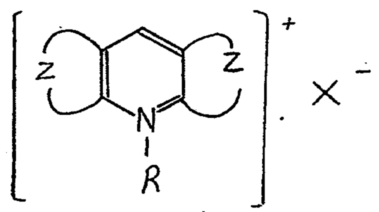
wherein R is selected from the group consisting of alkyl groups having not more than 20 carbon atoms and phenyl groups and X is a halogen atom selected from chlorine, bromine and iodine and either both of Z are nothing or each Z forms a further benzene ring.

4. An electro-optical device according to claim 6, wherein the liquid crystal layer contains 0.05 to 1% by weight of the halides of the organic quaternary nitrogen compounds, based on the weight of the liquid crystal.

5. An electro-optical display device comprising:

(1) a pair of supporting members at least one of them being transparent, whereby a dynamic scattering motion of a liquid crystal is observed through said supporting members:

(2) a layer of nematic liquid crystal containing a compound represented by the following general formula:



wherein R is a member selected from the group consisting of alkyl groups having not more than 20 carbon atoms and a phenyl groups and X is a halogen atom selected from chlorine, bromine and iodine and either both of Z are nothing or each Z forms a further benzene ring; dissolved therein in an amount effective to enhance said dynamic scattering motion of said liquid crystal, said layer being interposed between said supporting member;

(3) a first electrode for applying a pulsating electric field for generating said dynamic scattering motion to said layer, wherein a plurality of displaying segments are formed by said first electrode in said layer;

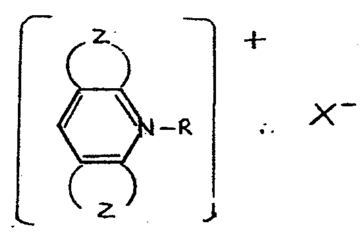
(4) a second electrode for applying said pulsating electric field in cooperation with said first electrode, said first and second electrodes being formed on the inner surfaces of said respective supporting members;

(5) a pulse generator for producing a pulse having an amplitude larger than a dynamic scattering motion limit but smaller than a discharge voltage of said liquid crystal and a pulse width smaller than 10 ms;

(6) means operatively connected to said pulse generator for selectively supplying said pulse to the selected electrodes of said first electrode and said second electrode in a predetermined order to the said selected electrodes with a predetermined time interval in order to apply said pulsating electric field to the selected segments corresponding to said selected electrodes thereby to generate said dynamic scattering motion in said liquid crystal of said selected segments, said time interval being shorter than a period in which an intensity of light scattering to be observed decays to a predetermined value.

6. An electro-optical device according to claim 5, wherein the liquid crystal layer contains 0.05 to 1% by weight of the halides of the organic quaternary nitrogen compounds, based on the weight of the liquid crystal.

7. A liquid crystal composition suitable for use in an electro-optical device which comprise a compound of the following formula:



wherein R is a member selected from the group consisting of alkyl group having not more than 20 carbon atoms and phenyl groups and X is a halogen atom from chlorine, bromine and iodine, and either both of Z are nothing or each froms a further benzene ring.

8. An electro-optical device comprising a liquid crystal composition substantially as described herein in any of Examples 1 to 8.

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1434275 COMPLETE SPECIFICATION

3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

FIG. 1

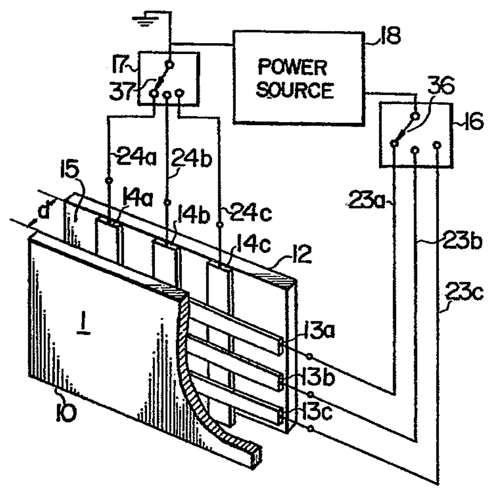


FIG. 2

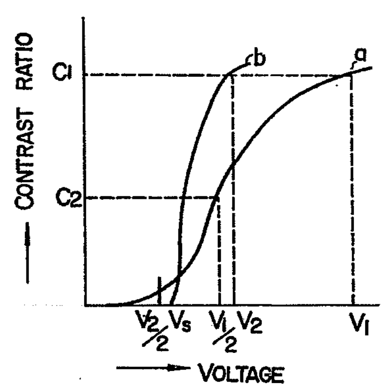


FIG. 3

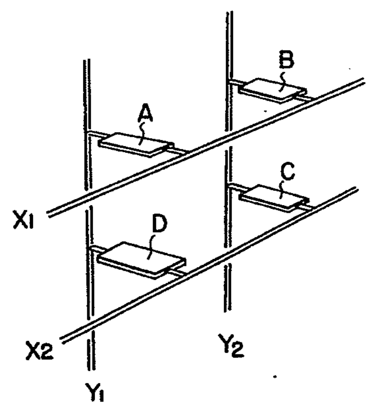

A
B
C
D
X1
X2
Y1
Y2

FIG. 4

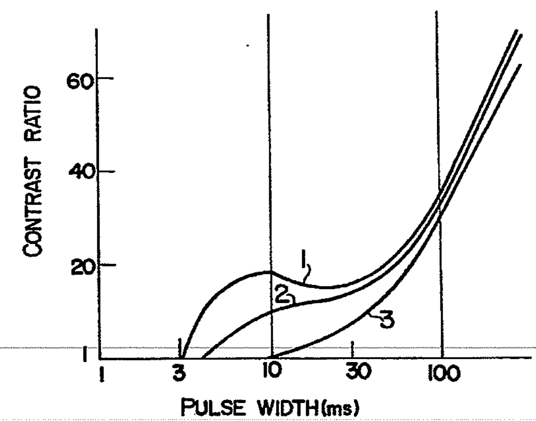

CONTRAST RATIO
60
40
20
1
1
3
10
30
100
PULSE WIDTH (ms)

FIG.5

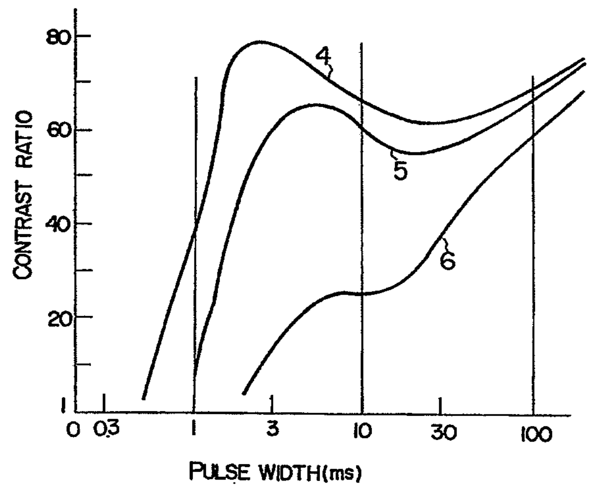
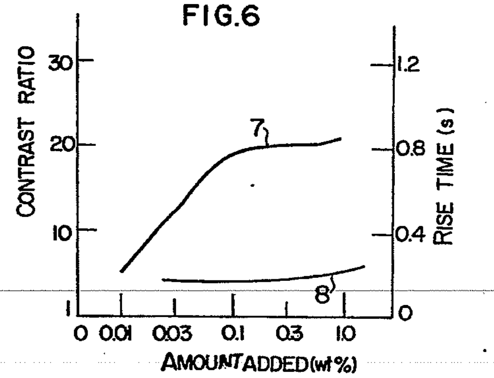

80
60
40
20
1
CONTRAST RATIO
4
5
6
0
03
1
3
10
30
100
PULSE WIDTH(ms)

FIG.6


30
20
10
1
CONTRAST RATIO
1.2
0.8
0.4
0
RISE TIME (s)
7
8
0
0.01
0.03
0.1
0.3
1.0
AMOUNT ADDED(wt%)